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Multiphoton Ionization Via an Excited State; A Survey of its Effect on Laser Breakdown in the Atmosphere

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CONTENTS

MULTIPHOTON IONIZATION VIA AN EXCITED STATE; A SURVEY OF ITS EFFECT ON LASER BREAKDOWN IN THE ATMOSPHERE

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Abstract

The program on controlled atmospheric breakdown at a distance depends on both the compression and focusing of the laser beam, and also on the breakdown mechanism. For normal atmospheric constituents and available laser wavelengths the ionization energy is much greater than the photon energy. If the laser pulse time is so short that avalanche breakdown cannot occur, other mechanisms are multiphoton ionization, or in the case of extremely high laser irradiance, tunneling ionization. For the laser pulse irradiances of interest in the ONR propagation program, it is the former mechanism that is the more likely one. However the more photons one needs, the more difficult it is to ionize. In this respect, ultraviolet photons are better than optical, which in turn are better than infrared. In this memo, we examine multiphoton ionization via the excitation of an intermediate state. Most experimental data indicates that the ionization does occur through an intemediate state both for nanosecond (ns) and femtosecond (fs) pulses. This makes ionization easier to accomplish than it might otherwise have been and is thereby of potential importance to the ONR program. This memo surveys some of the experimental data and also examines the theoretical basis for the frequent importance of multiphoton ionization via an intermediate state.

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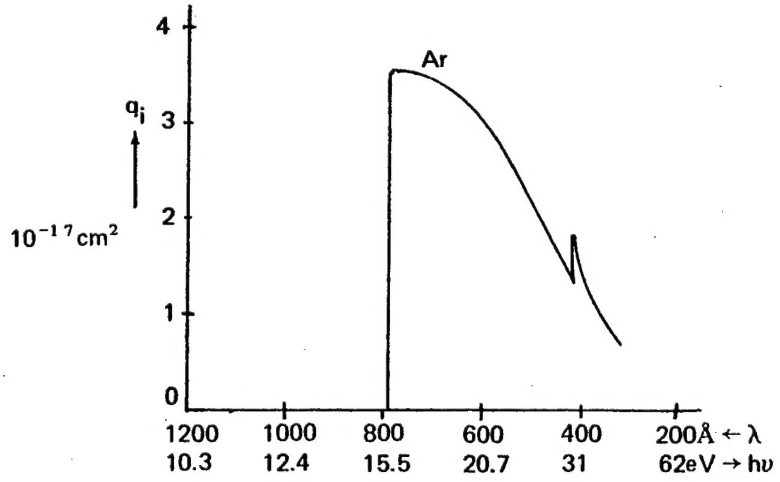
I. Introduction:

In the laser atmospheric breakdown project, a short (~100fs) light pulse is propagated through the atmosphere. If the pulse is properly constructed, it produces atmospheric breakdown at a controlled range. It does so by first compressing longitudinally due to its propagation in dispersive medium (the atmosphere), at which point the irradiance becomes sufficient for transverse self focusing, and thereby producing breakdown. This work addresses how that breakdown is produced once critical irradiance is achieved. Even at full atmospheric density, in 100 fs there is not sufficient time for avalanche breakdown. Whatever breakdown occurs is governed by the laser light and little else.

Here we examine in qualitative survey form an issue regarding this breakdown, specifically multi photon breakdown through an intermediate state. For the atmospheric constituents and likely laser wavelengths, the ionization energy is much greater than the photon energy. If $q = E_i/h\nu$, one would expect the rate of electron generation to scale as I^q where I is the laser irradiance. However, often the exponent is less than q. One explanation could be that there is an intermediate state of lower energy. The laser excites it, and then ionizes from this state. Some issues are what these intermediate states are, and the likelihood of the laser exciting through them. We examine these issues here in a qualitative way without getting into the details of the atomic and molecular physics. Our conclusion is that it is very likely that in the general case, multiphoton ionization through an excited state will be important.

II. Single Photon Ionization:

The key is that a photon can only ionize an atom or molecule if the photon energy is above the ionization energy. For instance the cross section for single photo-ionization of Argon looks like



Single photon photoionization cross section of argon

Figure 1

It hits its maximum at the ionization energy and then mostly decreases. The reason that the peak is broad is that excess photon energy is taken up only by the emitted electron; as best I can tell, there is no recoil photon at lower energy. This will be important for where there is an intermediate state. That is if we excite first to an intermediate state, since there is no recoil photon, and no recoil electron, the resonance width is quite narrow. We will spend a good bit of time shortly looking into this in more detail. However first, let's see what this means for single photon ionization of a gas. We have the equation for electron production by a laser

$$\frac{dn_e}{dt} = N\sigma_i J_{ph} \equiv N\sigma_i \frac{I}{h\nu} \qquad (1)$$

where N is the background neural density, J_{ph} is the photon flux, I is the irradiance and hν is the photon energy.

For the lasers we are talking about these are extremely fast ionization rates. Let's say I $=10^{12}$ W/cm^2. Then for a 1 eV photon with an ionization cross section like in Fig 1, we fully ionize the gas in about 2 femtosec! Of course this does not happen because the ionization energy of the gas is almost always well above 1 eV. However it does point out that photo-ionization is an extremely potent process if we had an energetic enough photon or a gas with low enough ionization energy.

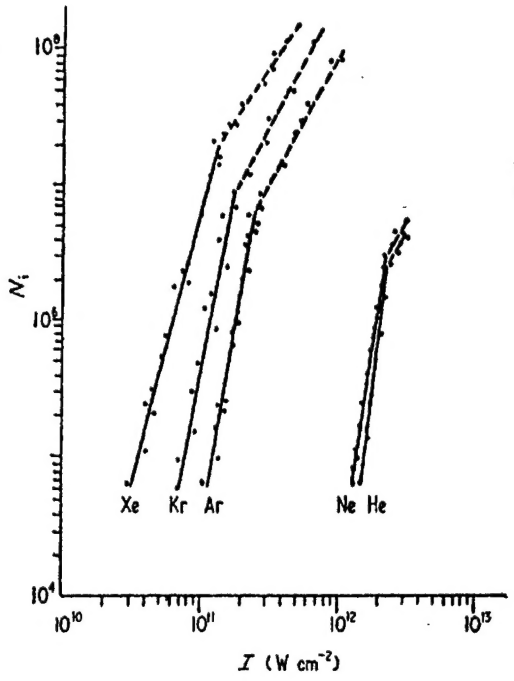
We will use this result to assume that in any multiphoton process, if resonant frequencies and widths shift around during the laser pulse, once an appropriate resonance is struck at a particular time in the pulse, ionization occurs extremely rapidly.

III. Some Data Relating to Multiphoton Ionization

If the photon energy is too low for single photon ionization, the next thing is multiphoton ionization. Here the electron production rate would be

$$\frac{dn_e}{dt} = \alpha\left(\frac{I}{I_o}\right)^q N \qquad (2)$$

where q is the number of photons required for ionization. Grey Morgan [2] has some data on this for the rare gases, but this is for 10 nsec pulses. The experiments he cites (done in Russia and France in the 1970's) focused the laser into an evacuated chamber with a pressure of about 10^{-2} torr, so that avalanche ionization does not occur on the relevant time scale. The photon energy of the laser light was 2.34 eV. Then the ions produced as a function of laser irradiance were measured. Shown below is his data:



Data on photoionization of the rare gases

Figure 2

Measuring the slopes (i.e. the q), and comparing with the number of photons needed to ionize as well as excite the lowest excited state, we find the table below.

Element	q	(E_i/2.34eV)	(E_x/2.34eV)	I_a
He	8	10.5	8.5	$1.2\text{x}10^{12}$
Ne	7.4	9.2	7.1	10^{12}
Ar	5.8	6.7	4.9	$8\text{x}10^{10}$
Kr	5.3	5.9	4.2	$5\text{x}10^{10}$
Xe	4	5.1	3.5	$2\text{x}10^{10}$

Here E_i is the ionization energy, E_x is the lowest electronic excitation energy, and I_a is the irradiance if we use the formula for ions produced

$$N_i = 10^4 \left(\frac{I}{I_a} \right)^q \qquad (3)$$

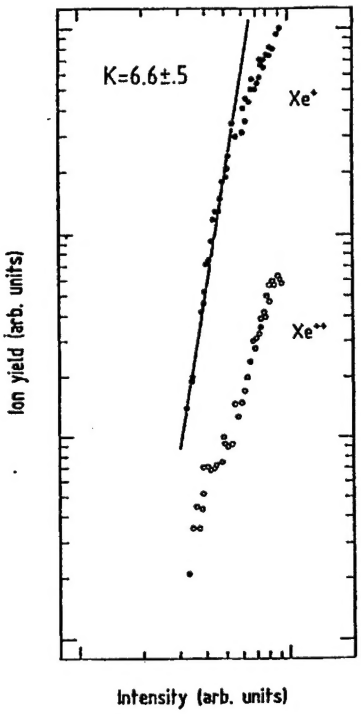
Notice that in all cases it seems to take fewer photons than one might think to ionize the atom. In fact, for He, Ne and Xe, the agreement is rather good for excitation, not ionization. For argon and krypton, it is in between.

Before going to excitation, it is worth looking into whether we can pick an α and I_o in Eq. (2) which agrees reasonably well for all multi-photon excitation processes, including single photon ionization. For this to be so, the power law part on all curves would have to meet at or near one point on the graph. This is not the case. Using He and Xe, we would find that

$$N_i = 10^4 \left(\frac{I}{5 \times 10^{13} W/cm^2} \right)^q \qquad (4)$$

works for both. However finding a single relation for argon and helium, the denominator in Eq. (4) would be 5×10^{15} W/cm^2. Thus, as useful as it would be to find a single relation for all or most gases, it does not appear to be feasible. I have also tried to fit the single photon ionization onto such a formula. However from the data given in the experimental references, it is not very clear how to do this. For instance Grey Morgan does not give either absolute measurement of ions produced (except to speculate that the knees in the curves are from fully ionizing the gas around the focal spot). Also he does not give focal parameters for the laser. Taking what seem to be reasonable guesses for all of these, I could not get Eq. (1) into a form like Eq. (2) with an α or an I_o which agreed with the Grey Morgan data.

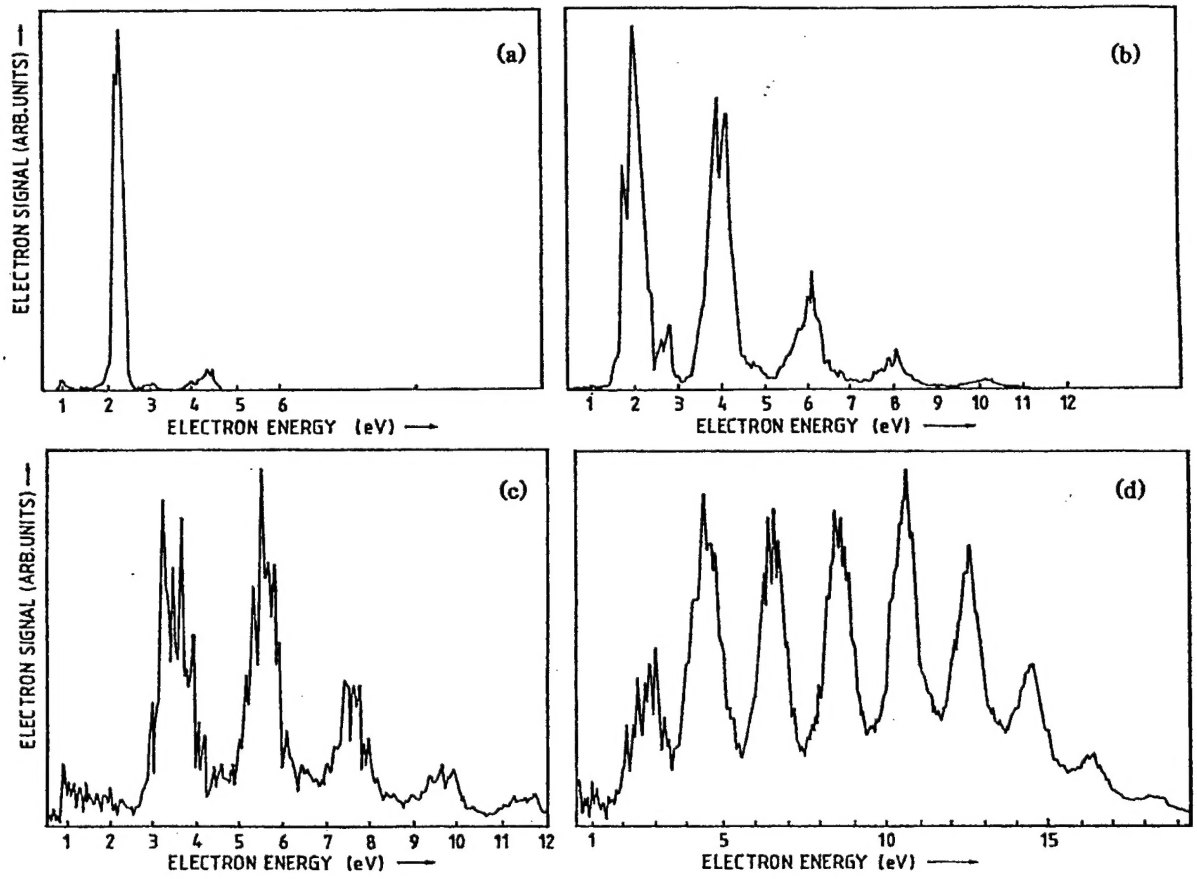
The experiments cited so far were with 10 ns laser pulses. What about 100 fs pulses? Muller et al [3] examine this. They use a 100 fs laser to ionize Xe at very low gas pressure (which they do not give) with 2 eV photons. Their q is not in accord with the 10 ns data. Shown below is their curve for relative number of ions, and their q is 6.6±0.5. This is even higher q than what one would need for direct multi-photon ionization.



Photoionization of Xe with 100 fs laser pulses

Figure 3

However their irradiances were considerably higher than in the Grey Morgan data, the former being around 10^{14}, the latter being around $10^{11} - 10^{12}$ W/cm^2. Muller observes above threshold ionization (ATI) in his experiment. What this means is that the electrons are not kicked out of the atom with an energy just $q\hbar\nu - E_i$, but rather, the electron may absorb more than the minimum number of photons necessary to ionize. Muller gives measurements of this, the ATI increases rather rapidly as a function of irradiance. Below are his measured energy spectra as functions of total laser energy:



Electron energy spectrum measured after multiphoton ionization of xenon with 2 eV photon pulses of 100 fs duration. The pulse energies are a) 11μJ, b) 24μJ, c) 29μJ , d 35μJ .

Figure 4

Clearly, depending on the amount of ATI, as the irradiance increases the ultimate effect is a mixture of a larger and larger combination of q's. For instance, it takes about 4 photons of 2 eV to reach the first excited state of xenon. From there it would take 3 photons to reach the 2 eV lowest energy electron state in Fig. 4a, so the we would expect the process to go like a 4 photon process. However it would take 7 photons to go from the excited state to the 10 eV higher electron energy state in Fig 4d, so we might expect it to have the characteristics of about a 7 photon process at the highest pulse energy, as seems to be the case. However to get to the 10 eV photon directly from the ground state would take 11 photons; many more than what Muller

measures. Thus it seems that ionization from intermediate states plays an important role in Muller's data as well, but it is not clear how one gets a single exponent if ATI plays an important role. Nevertheless Muller is in all likelihood operating at a considerably larger irradiance (his I ~ 10^{14}W/cm^2) than we plan to in our atmospheric propagation studies.

IV Excitation through an Excited State:

As we have seen at least in the data Grey Morgan presented, the number of photons generally agrees reasonably well with the number needed to excite the atom. Then, if there is no ATI, once the atom is excited, say by q' photons, it is very easily ionized in a fewer photon process because the excitation energy is typically about three quarters of the ionization energy. Grey Morgan, Keldysh [4] and a book by Federov [5] discuss this.

Let us look at the simplest dynamics of exciting via an excited state. We will use no subscript for the ground state, x for an excited atomic state, and i for the ion. Let us say that the excited state decays back to a lower state, which we assume for convenience is the ground state. Assuming all excitation is via the excited state, the rate equations are

$$\frac{dN}{dt} = -\alpha_x \left(\frac{I}{I_o}\right)^{q_x} N + \nu N_x \tag{5}$$

$$\frac{dN_x}{dt} = \alpha_x \left(\frac{I}{I_o}\right)^{q_x} N - \alpha_i \left(\frac{I}{I_o}\right)^{q_i} N_x - \alpha_x \left(\frac{I}{I_o}\right)^{q_x} N_x - \nu N_x \tag{6}$$

$$\frac{dN_i}{dt} = \alpha_i \left(\frac{I}{I_o}\right)^{q_i} N_x \tag{7}$$

where we have assumed the rate of stimulated emission in Eq. (6) is equal to the rate of excitation. For single photon processes, this means the states have equal statistical weights. Since the excitation energy is generally well over half the ionization energy, we expect $q_x > q_i$. Hence once a state is excited, it is quickly ionized, implying that the excited state is in steady state. Making this assumption , we find that

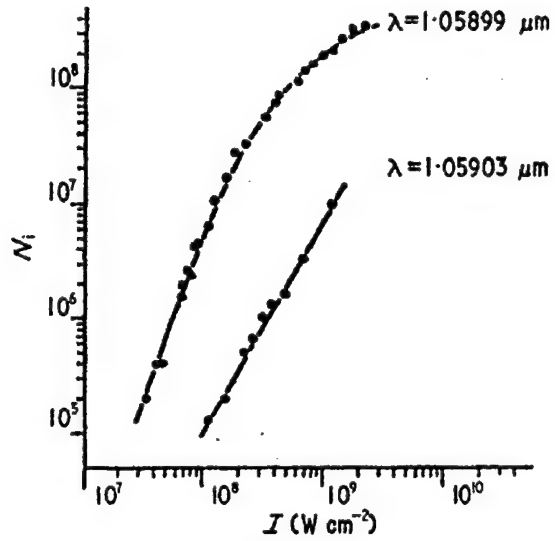
$$N_x = \frac{\alpha_x \left(\frac{I}{I_o}\right)^{q_x} N}{\alpha_i \left(\frac{I}{I_o}\right)^{q_i} + \alpha_x \left(\frac{I}{I_o}\right)^{q_x} + \nu} \tag{8}$$

Assuming the dominant term in the denominator of Eq. (8) is the ionization term, then we find that

$$\frac{dN_i}{dt} = \alpha_x \left(\frac{I}{I_o} \right)^{q_x} N \qquad (9)$$

so the ionization rate is the excitation rate, and it depends on a lower power of I/I_o. Thus if the ionization is through an excited state, we would expect the ionization to be much easier.

The problem is that that all of the authors say that the laser has to be tuned rather precisely to the intermediate state, that is $E_x = ph\nu$ where p is an integer, to rather high accuracy. This might happen, but the authors of refs [4 and 5] regard this as a coincidence. For instance Grey Morgan shows data for multi-photon ionization of a cesium atomic beam with a tunable laser. In Figure 5 is his data for multi-photon ionization of cesium atomic beam with a tunable laser. For one of the laser wavelengths, there is an almost exact resonance with a three photon excitation. His data is for ionization by lasers of two wavelengths different by only four parts in 10^5. Clearly ionization is strongly affected by wavelength here.



Data for photoionization of Cs for two laser wavelengths

Figure 5

In the light of Fig 5, is it reasonable that q is governed by excitation level even if the laser is not perfectly tuned?

V. Number and Width of Transition Lines:

There are several other reasons to think excitation through an excited state is often important. First, let us look at the effects of number of participating states, which are quite different for rare gases and alkali metals, and then let us look at the width and shifts of the transition line.

Let us start with the number of possible transition lines. For a hydrogen atom, there are 2 possible l=0 ground states, with positive and negative electron spin. There are 8 possible first excited states, 2 with l=0 and 6 with l=1. For a hydrogen atom, they are all degenerate except for the spin orbit coupling. If the nuclear and self consistent electron potential is a central potential, the l=0 states are no longer degenerate with the l=1 states, but they are degenerate with each other. If there are deviations from spherical symmetry in the self consistent potential, none of the states are degenerate. For the next excited states, there are 18 states, all of which are degenerate for a bare nuclear potential; the s, p and d states are degenerate among themselves for a central self consistent potential; and these would in general be non degenerate for a non central potential.

In an alkali metal, there is a single electron outside a closed shell and its energy is well above that of the inner electrons. It is reasonable to think that any single or multiphoton process will excite only that the outer electron, so we would expect multiphoton processes to proceed among a relatively small number of intermediate states, because they are all governed by a single valance electron. Contrast that with say argon which has a closed shell consisting of many electrons. If the self consistent potential is nearly like the bare nuclear potential, or is nearly a central potential, there could be a large number of possible transitions, of nearly the same energy, involving any one of a number of the outer shell electrons. Thus we expect that an alkali metal may require a much more finely tuned photon because it has fewer possible intermediate states. This seems to be consistent with Grey morgan's data on rare gases and alkali metals.

Second let us consider the widths of the possible transition lines. To start consider the width of the laser line, τ^{-1} where τ is the laser pulse width. For the 10 ns data presented by Grey Morgan, the width is $10^{-8}s^{-1}$, or a relative width of about $2x10^{-8}$ for his 2 eV photons. Thus we do not expect laser bandwidth to be significant in this case. However for 100 fs pulses, the relative bandwidth increases to about $2x10^{-3}$ which can now be significant. This is a broadening of 0.02 eV for a 10 eV transition. If there are 50 possible transitions, the total width could be as high as 1 eV. Thus laser bandwidth could play an important role for 100 fs pulses, but not for 10 ns pulses.

Now let us consider the width of the transition lines themselves. This is an extremely complicated issue, especially in gases or plasmas, books have been written about it [6]. We will look at only the simplest aspect, and one dominated by the high power laser. As we have formulated the theory, the denominator of Eq. (8) is the line width. There are three terms in it, the inherent line width ν, governed by spontaneous downward transitions; $\alpha_x(I/I_o)^{qx}$, governed by stimulated transitions; and $\alpha_i(I/I_o)^{qi}$, governed by ionization. The natural line width is typically of order $10^{-6}\omega_L$, where ω_L is the laser frequency. This is also the order of the Doppler width and

pressure broadening of air at room temperature [7]. Thus these widths by themselves are insufficient to explain Grey Morgan's data unless there are something like 10^5 possible transition lines a few eV down from the continuum.

Let us consider the other two effects. First of all, note that the laser irradiance in Fig 5 is quite low compared to what we think of as irradiance for a laser self focused in the atmosphere, 10^{11} – 10^{13} W/cm^2. Therefore it might be that an irradiance dependent broadening could be responsible for the differences in the wavelength sensitivity of Fig (5) and the possible wavelength insensitivity of Fig (2). Let us estimate these contributions to line width. First consider the stimulated two photon emission. This is also approximately equal to the ionization rate if our steady state assumption is valid.

We estimate this rate by assuming that the self focused laser successfully produces an ion density of $3x10^{17}$cm^{-3} in 100 fs. If the atmospheric density is $3x10^{19}$ cm^{-3}, then the stimulated decay rate is $\nu_{st} \sim 10^{11}$. This would give a line width of about $3x10^{-5}\omega_L$ if the photon energy is about 2 eV. This is a considerably larger line width than the spontaneous, Doppler or pressure broadened line width, but most likely still too to bring a nonresonant line into resonance. Furthermore, we estimated this width for 100fs laser pulses in full atmosphere. For Grey Morgans rare gas data, where he produces perhaps 10^{15} cm^{-3} electron density in 10^{-8} s, the width is many orders of magnitude lower.

However the basic assumption to justify the steady state theory was that the ionization rate from the excited state, which required many fewer photons than the excitation, proceeded at a much faster rate than the excitation. This ionization rate is the last term in the denominator of Eq. (8), and we expect it to be the dominant term. From only the knowledge of the number of electrons generated in 100 fs, without knowledge of the α's, I_o's and q's, we cannot easily estimate all of these rates. However for 100 fs pulses, ionization broadening by as much as $10^{-3}\omega_L$ or even higher is not unreasonable to expect. It is difficult to estimate what the width would be for 10 ns pulses. In all likelihood it would be much less, but if the ionization rate from the excited state is *very* much larger than the excitation rate, it could be significant here as well. Thus, the intense laser appears to have a large effect on the line width, especially for short pulses.

There is another physical process which could also enhance excitation and this is the AC Stark shift. Federov discusses this. In an oscillating electric field, a bound electron can emit and absorb virtual photons, and this gives rise to a frequency shift. This gives rise to an energy shift of the n^{th} level given by

$$\delta E_n = -\frac{1}{4}\chi_n(\omega)\varepsilon^2 \qquad (10)$$

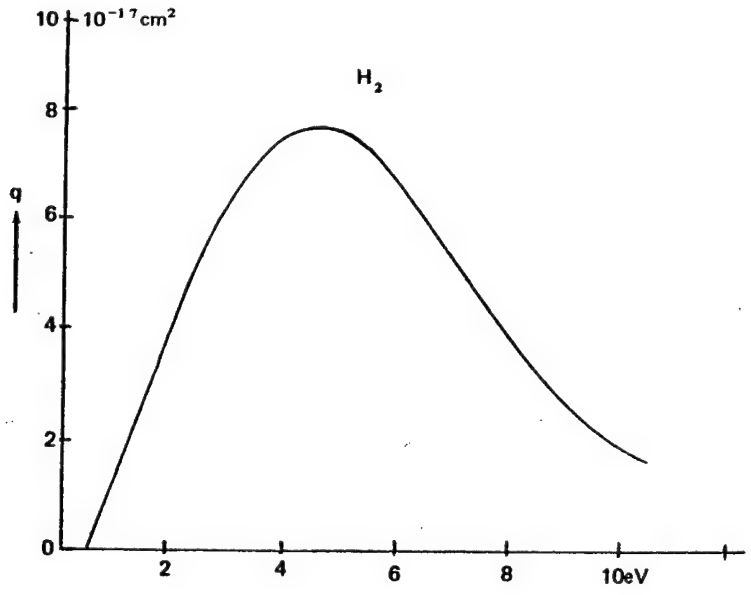
(Eq. (1.3.17) of Federov) where χ is what he calls the dynamic polarizability of that level and ε is the electric field. For high Rydberg levels, δE_n works out to be the classical quiver energy in the oscillating electric field, he does not give a result for low levels, but let's take this as a guide. Then at an irradiance of 10^{12} W/cm^2, the energy shifts are of order 0.035 eV, or a width of 0.35 eV at 10^{13}. The latter is certainly a significant width, and the former might be if there are a

sufficient number of intermediate states. Furthermore, the lower lying states may have larger χ's. Now as the laser field increases from zero to its maximum, the atomic levels shift by about this energy. Therefore at some time during the laser pulse, if the energy mismatch is not too great, the AC stark shift could well bring the levels into resonance at some point during the pulse. This effect does not depend on the laser pulse width, but only on its irradiance.

With the combination of ionization broadening, and AC Stark shift, for I in the range of 10^{12} W/cm^2, (and even more so if I is as high as 10^{13} W/cm^2), and a large number of possible transition lines of energies not too different from one another; it seems quite reasonable to think that the number of photons for the process is approximately that required for atomic excitation, not ionization. This makes ionization with an intense laser easier to accomplish than if one had to directly ionize without coupling through an intermediate state.

VI Atoms and Molecules

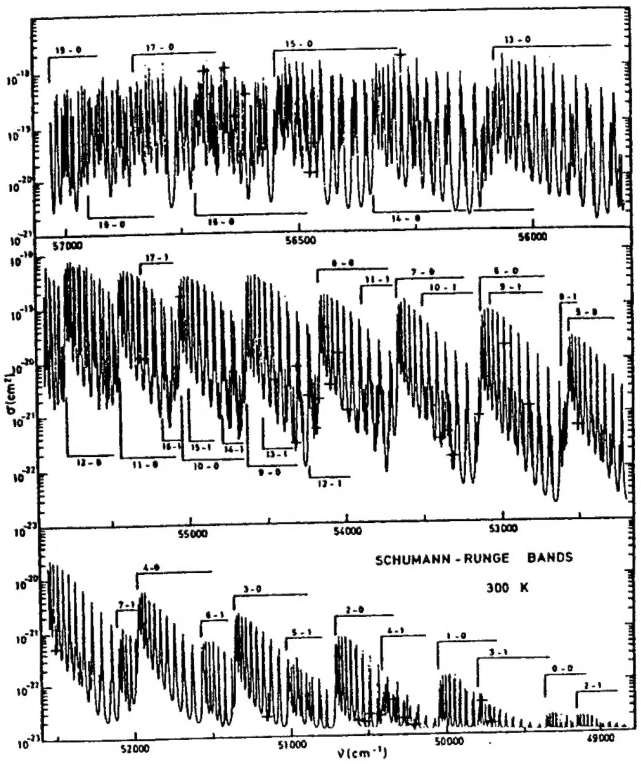
So far we have been talking only about atoms. What about molecules? These have many more excited states levels because there are low level rotation and vibration states as well as electronic states. Shown schematically in Fig 6 is the excitation cross section for the hydrogen molecule as a function of incident electron energy.



Coarse figure of the excitation cross section for H_2

Figure 6

The individual transitions are not shown, but they are rather dense compared to the electronic states. For instance Fig 7 shows the Schumann-Runge transitions for O_2 between 1750 and 2050 angstroms in the uv. The large number of rotation lines is evident. Clearly, in some cases there can be an enormous number of intermediate states for molecular gases.



The Schumann Runge transitions for O_2

Fig 7

The question is whether these rotational and vibrational states can serve as intermediate states. If they could, the laser the laser might be able to ionize the molecule with a long cascade of (say) single photon transitions. Grey Morgan discusses two experiments on molecular systems. With a cesium beam again, about 0.25% of the beam atoms combine to form cesium molecules. He cites an experiment showing ionization via a two photon process of exciting a vibrational state of the atom. He also cites an experiment on multi-photon ionization of hydrogen molecules with a neodymium laser. For direct photo-ionization, one would require a q of 13. However by accessing various vibrational and electronic states, they could achieve photo-ionization with q's ranging from 6 to 11. Thus, from this data, it seems as if vibrational states may also serve as

intermediate states for ionization, but only if their energy is not too far below the ionization energy.

Keldysh also points out that molecules may be more easily ionized through an intermediate state. Recall that the reason for the sharp resonance is that there is no recoil photon. However in a molecule, Keldysh point out that the recoil energy can go into internal states of the molecule, vibrational or rotational states. Thus, for multi-photon ionization of a molecule, it seems almost certain it can be done via the lowest level electronic transition in the molecule.

VII. The Energy to Produce Ionization.

In the laser codes developed [1], one important parameter is the energy to produce an electron ion pair W_i. In the codes this is taken as the ionization energy E_i. In conventional discharges, the energy to produce an electron ion pair is always much larger. A conventional discharge creates electrons at low energy, and then as they are added to the electron fluid, the electrons are heated by the electric field. Electrons lose energy not only to ionization, but also to all excitations. Since these excitations have energy below the ionization energy, and the electron temperature is almost always low compared to the ionization or excitation energy, the tail of the distribution function (whether Maxwellian or not) does the ionization and excitation. Since this tail falls off considerably between the excitation and ionization energy, most of the energy is lost to excitations, and $W_i >> E_i$. The values of W_i are tabulated in papers on electron swarm data, for various types of discharges. Clearly, the higher the discharge temperature, the lower W_i gets. The ultimate example is ionization by an electron beam. Since at the beam energy, the ionization and important excitation processes all have about the same cross section, for beam ionization, W_i is typically 2 to 3 times E_i, and beam ionization is regarded as very efficient.

In laser ionization, the question is what energy is wasted in the ionization. Multiphoton ionization appears to be a rather efficient process. The excitations which constitute the wasted energy in avalanche or electron beam ionization are important stepping stones in multiphoton ionization. As we saw in our discussion of single photon ionization, if it goes, it goes fast. Thus once an atom or molecule is excited, it should be ionized very quickly, certainly before it has a chance to decay. This is the basis of the steady state approximation we have been using However for the case of an atom, there may be ionization through the excitation of an electron not in the highest energy state. Once it is ionized, the ion is left in an excited state, and this energy is ultimately radiated away and lost. Furthermore, in the case of a molecule, there may be a recoil in a vibrational or rotational state, and this energy is lost as well. Also, it may be that certain intermediate states cannot be excited to ionization for one reason or another. Finally there is energy lost to ATI if the irradiance is high enough, although this is not strictly speaking lost, but resides in the plasma electron temperature. To summarize, the multi-photon ionization process, proceeding through an intermediate state, would appear to be quite efficient, but the efficiency is still less than 100%. In the codes, if we take $W_i = (1.5 - 2)xE_i$, this is probably a reasonable approximation.

VIII. Effects on the NRL Experimental and Theory Program

One immediate conclusion for the NRL experimental program, which has as its goal producing atmospheric breakdown, at a distance, in a controlled fashion, is that the higher the photon energy, the easier this is to do. Thus if we can double or triple the laser frequency, we would probably much more than make up for the energy lost there with much greater ease in ionizing the atmosphere at the focal point. Almost all of the experiments I cited used photon energies of 2 or more eV.

Regarding the simulations, the knee in Fig. 2 is attributed to saturation. That is (since the gas density is less than the critical density) fully ionizing the focal area of the laser. Then presumably the laser refracts out and ionizes other regions, but less effectively. It seems that this is something we could test rather easily with the existing codes. The simulations would be especially easy because all of the experiments were done at very low pressure, so that all of the complicated effects of the neutral atmosphere, Raman effect, turbulence, etc would not be present. We could specify an ionization of the form of Eq. (2), $W_i = 2E_i$ and see if we could reproduce something like Fig 2. It seems that this would be a good and not too difficult way of benchmarking our codes. If we could do this, the code would probably be more convincing, both to ourselves and to others.

IX. Conclusions

Based on examination of the evidence, it seems likely that multi-photon ionization proceeds through an intermediate state. This state is most likely the lowest electronic state of the atom or molecule. For instance if for the particular atom and photon, $q = 9.3$ for ionization, and $q = 6.4$ for the lowest excitation, then probably $q = 7$ is about the best choice to use in Eq. (2). It does not appear that there is any universal α and I_o to use in Eq. (2). One must pick a value for each atom or molecule and photon energy. At sufficiently high irradiance, between the large number of intermediate states, ionization broadening of the transition line and the shifting of energy levels with laser irradiance; it seems very likely that in nearly all cases an intermediate electronic state will be available to boost multiphoton ionization. The shifting of the line frequencies depends only on the laser irradiance. The width depends on the pulse time as well. The broadening is almost surely important for 100 fs pulses, but is much less likely to be important for 10 ns pulses. Multi-photon ionization through an intermediate state seems to be a rather efficient process; $W_i = (1.5\text{-}2)xE_i$ is probably a reasonable approximation. For the experimental part of the program, it seems that controlled atmospheric breakdown at a distance is best accomplished by using as high a photon energy as possible. Finally, there seem to be tests we can do now to benchmark our simulations against earlier experiments on multiphoton ionization.

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